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THERMOELECTRIC POWER GENERATION

A RESEARCH AND DEVELOPMENT
PROGRAM ON MATERIALS AND
FABRICATION TECHNIQUES

QUARTERLY REPORT NO. 5
MAY 15, 1963

DIRECT ENERGY CONVERSION OPERATION
GENERAL ELECTRIC
950 WESTERN AVE., LYNN; MASS.

RESEARCH AND DEVELOPMENT
OF
MATERIALS AND FABRICATION TECHNIQUES
FOR
THERMOELECTRIC POWER GENERATION

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GENERAL ELECTRIC COMPANY
DIRECT ENERGY CONVERSION OPERATION
950 WESTERN AVENUE, LYNN, MASSACHUSETTS

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INTRODUCTION

This fifth quarterly report describes the cartridge development effort during the period January 1, 1963 to May 15, 1963 as funded by the Bureau of Ships under Contract NObs 86854.

Section I is a continuation of the cartridge fabrication and evaluation program. Section II is a summary of the effort accomplished to date and includes recommended future action.

SUMMARY

This report is intended to serve two purposes:

1. To describe progress in cartridge development during this report period.

2. To summarize all effort to date and to recommend future action.

Attention has been focused upon the iron end cap bonding problem. The two techniques outlined in the previous report, namely, isostatic bonding and tin telluride brazing, have been explored in some detail. Results obtained with tin telluride brazing, although not conclusive, show low electrical resistance and the presence of inclusions in the vicinity of the bond. Temperature testing of elements with tin telluride brazed end caps has resulted in fractures in the "P" type element and in some cases separation from the iron end caps. The isostatic bonding of iron end caps has shown that low resistance joints may be obtained in this manner as measured in several of the specimens.

Before continuing with this development effort, the progress to date must be carefully reviewed. The majority of cartridges fabricated produced power initially but experienced degradation with time while in operation. There were no abrupt failures in power output which reflects favorably upon the electrical and mechanical integrity of the package. From the techniques explored in bonding iron diffusion barriers, hot pressing provided elements most nearly approaching design power output.

It is believed that a concentrated effort in improving the mechanical properties of PbTe and a provision for stress-free assemblies will provide a more reliable package for thermoelectric power generation.

SECTION I - CARTRIDGE DEVELOPMENT & EVALUATION

I-1 Bonding Iron Diffusion Barriers

The previous report described two approaches to the iron end cap bonding problem; namely, SnTe brazing and gas pressure bonding. The bonds obtained, although somewhat encouraging, did not entirely provide the desired results. Primary among the stated objectives was the requirement for a low resistance electrical interface between the diffusion barrier and the lead telluride elements which would also provide a mechanically sound bond when subjected to temperature cycling. Measurements clearly show that an $r/\rho = 0.05$ cm may be obtained, but the mechanical integrity of the bond during operation is questionable.

Gas Pressure Bonding of diffusion barriers has been attempted with autoclave facilities at Battelle Memorial Institute. A capsule method of material confinement resembling the thermoelectric cartridge represented the first attempt.

An examination of the capsules after processing indicated that some buckling in the sleeve had occurred. This was anticipated but to a lesser degree than had actually taken place. In a number of samples, cracks in the sleeve accompanied buckling and resulted in the leakage of PbTe through the container walls.

It is now believed that an extremely close fit between sleeve and PbTe in the order of $\pm$ 0.001 inch with pre-indentations in the sleeve to promote uniform buckling would have prevented mechanical failure.

Density measurements on material salvaged from the experiment show that theoretical single crystal density was nearly obtained in a number of the samples. In cases where no PbTe leakage took place, an apparent good bond between iron and lead telluride was obtained.

Measured values of the Seebeck coefficient and electrical resistance on a number of samples are tabulated below. It will be noted that there is considerable variation in these values from specimen to specimen indicating that they were not subjected to uniform heating in the autoclave.

Measurements of Seebeck Coefficient & Resistance
Isostatic Bonding - Battelle

Specimen	Type	Seebeck Coefficient $\mu v/^{o}C$	Resistance $\mu\Omega$ (over all)
*3M (As Received)	P	64	525
*3M (As Received)	N	152	650
#1	P	66	2075
#1A	P	83	3325
** #2A	P	132	1675
#4	N	72	175
** #4A	N	87	317
#6	N	74	300

* Measured values of PbTe (1/2" D - 1/2" L) received from 3M for comparison with autoclave processed material.

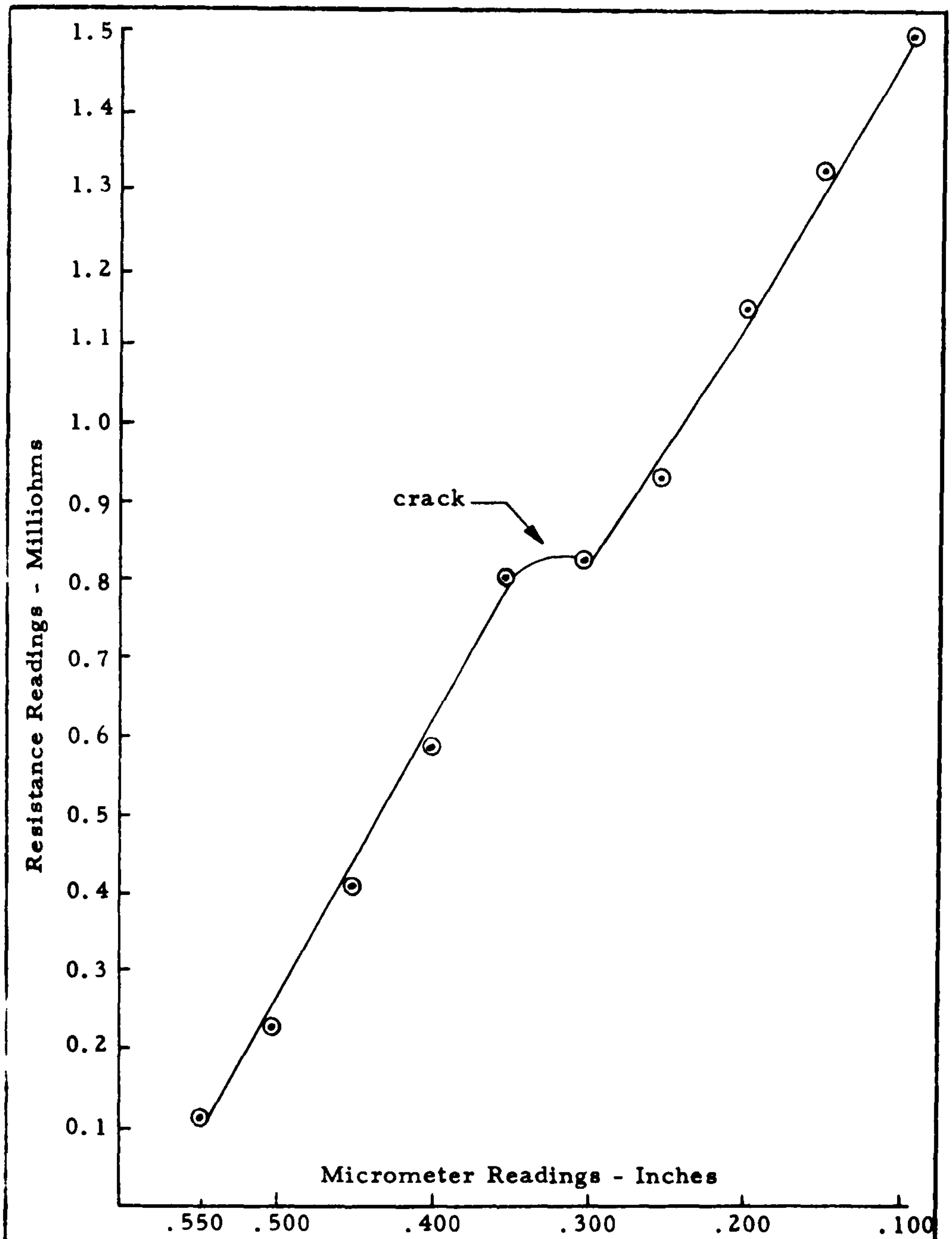
** Measurements performed by A. T. L. - G. E. Schenectady.

In the "N" type specimens, both the Seebeck coefficient and resistance decreased, indicating an increase in doping level. It is also believed that some excess lead was quenched into the lattice when the autoclave was cooled.

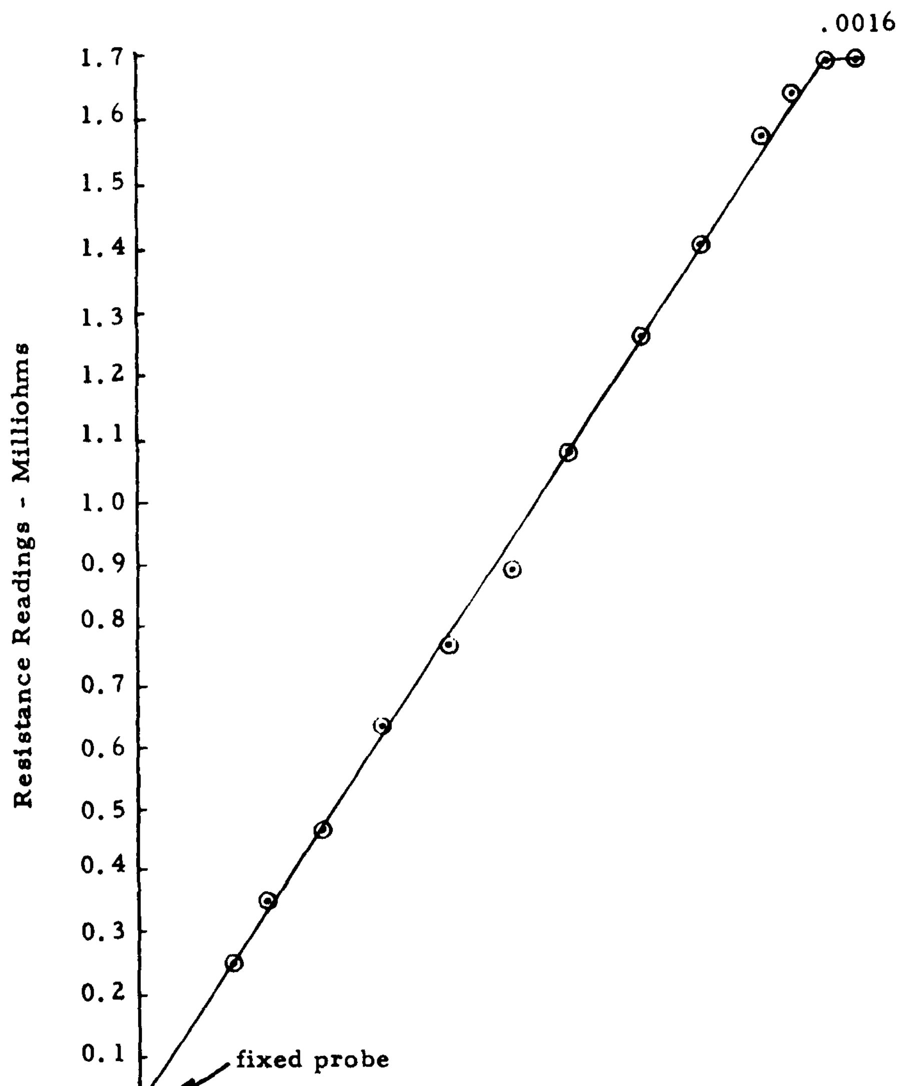
The "P" type specimens show higher Seebeck coefficients, indicating some loss of doping, and is indicated most noticeably in specimen 2A. Since the doping agent is sodium, it is possible that the doping loss was due to reaction with the mica sleeve which surrounds the PbTe billet. The high resistances are probably due to inclusions in the material or large voids in the vicinity of the iron end caps.

The resistances of specimens 4A and 2A were profiled, and plots of the results are shown in Figures 1, 2 and 3. For specimen 4A the results indicate little or no junction resistance, although an anomalous resistance point was obtained on the iron at one end of the specimen. As the plot indicates, the resistivity of the material was fairly uniform, and approximately half as great as the resistivity of material not subjected to isostatic pressing.

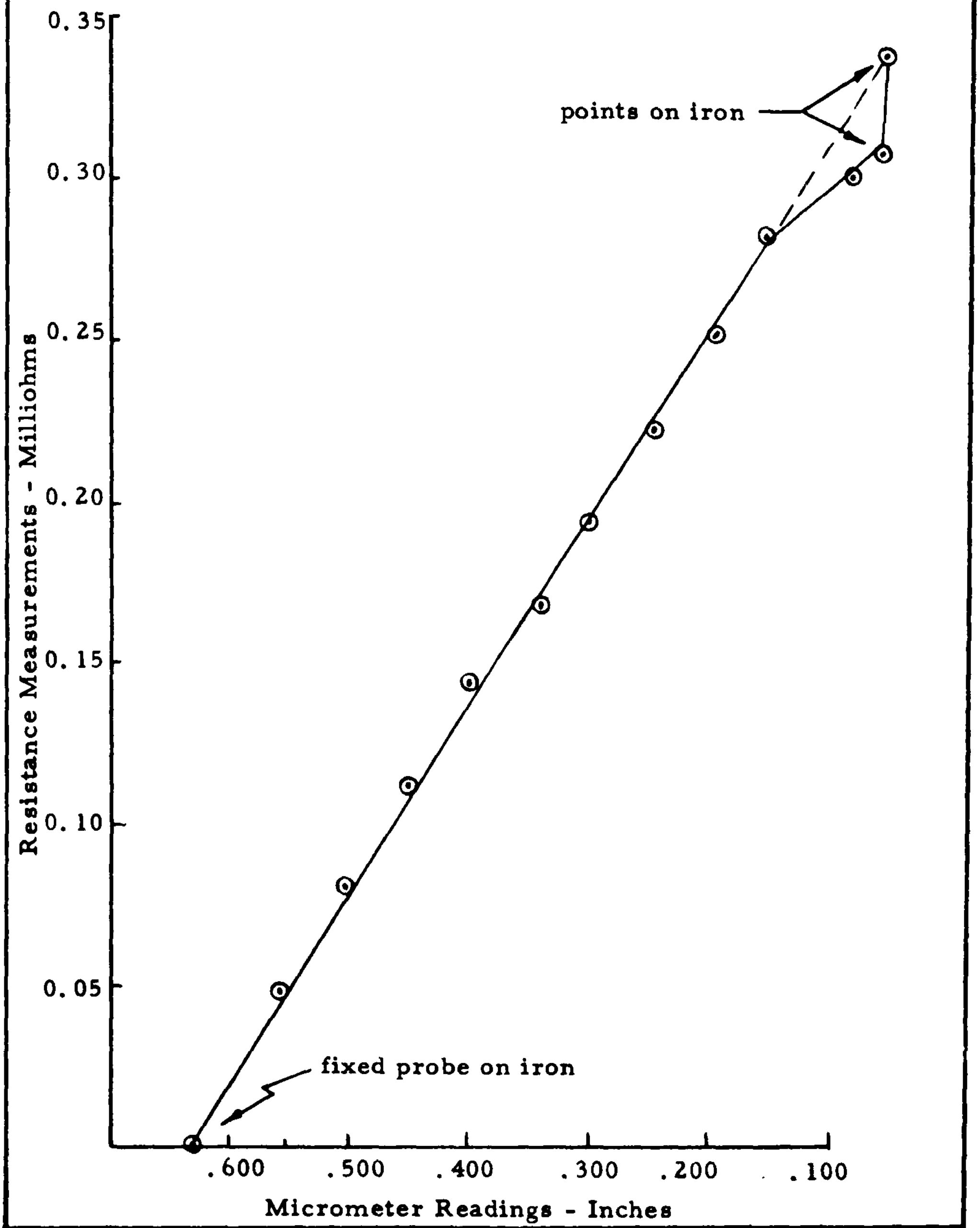
In the first profile of specimen 2A (Figure #1, page 7), a resistance anomaly appeared in the center of the specimen. In this profile it was impossible to secure points on the iron end caps. The measurements were repeated along another track, and in the second profile (Figure 2, page 8) the end points refer to points on the iron.



Advance Engineering DECO - G.E. Co. Lynn, Mass.	<u>FIGURE 1</u> Resistance Profile #1 Autoclave Processed 2A "P" Type	Quarterly Report #5 Contract NObs 86854 D. J. Gibson 5/15/63



Advance Engineering DECO - G.E. Co. Lynn, Mass.	FIGURE 2 Resistance Profile #2 Autoclave Processed 2A "P" Type	Quarterly Report #5 Contract NObs 86854 D. J. Gibson 5/15/63



Advance Engineering DECO - G.E. Co. Lynn, Mass.	FIGURE 3 Resistance Profile Autoclave Processed 4A "N" Type	Quarterly Report #5 Contract NObs 86854 D.J. Gibson 5/15/63

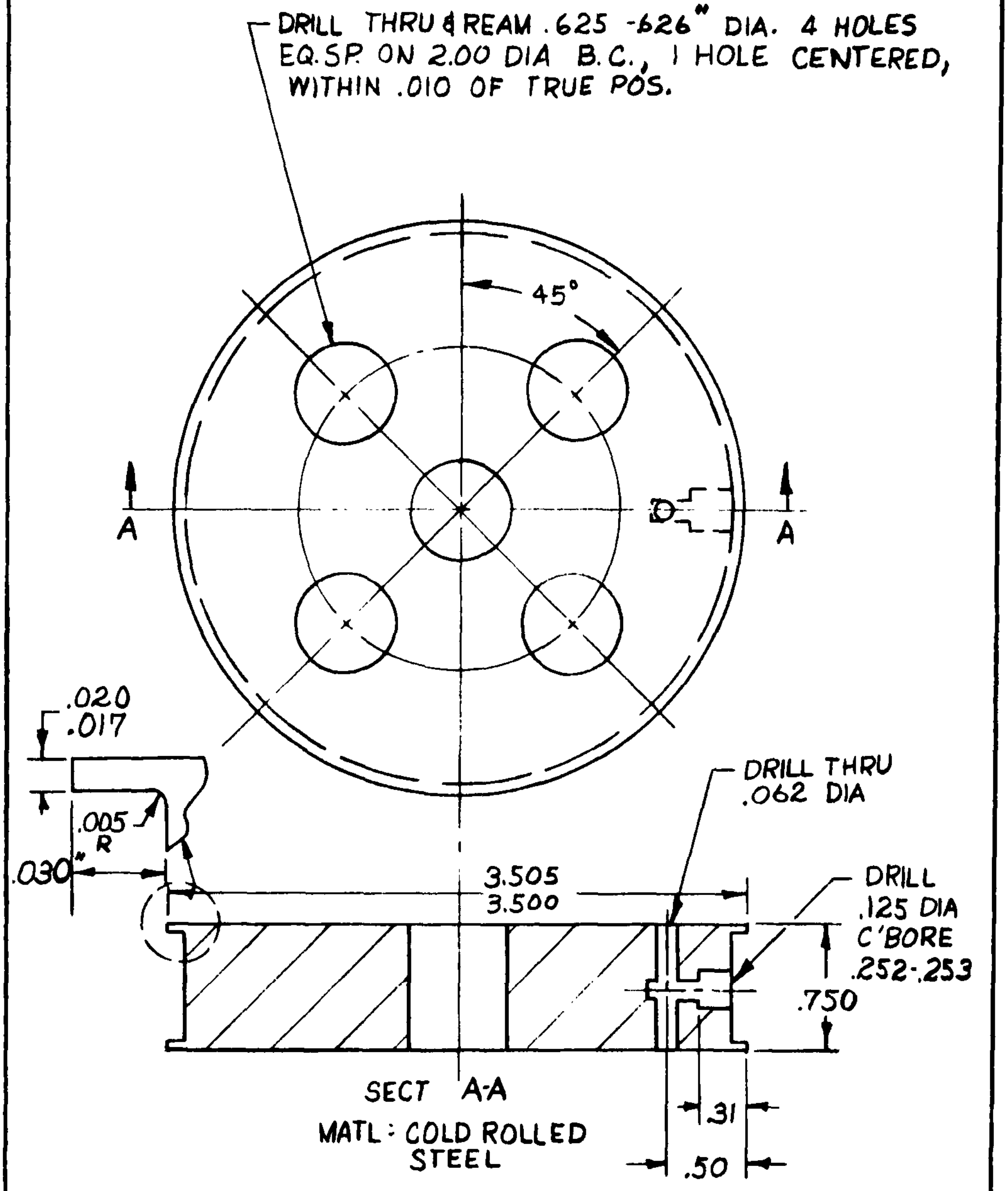
The low resistance region in the center of the first plot was not found in the second and is believed due to an inclusion in the surface of the piece. Again, the bulk resistivity of the material appears to be uniform, but at this time on the curve it is higher rather than lower than the resistivity of the unpressed material.

In order to avoid buckling problems inherent in the original capsule approach, a flat plate with drilled holes for PbTe billet insertion will now be used for experimental purposes. Figures 4 and 5 on pages 11 and 12 show the material receiver plate and assembly with welded cover plates. After the assembly and welds are complete, air evacuation is effected by means of a pinch-off tube.

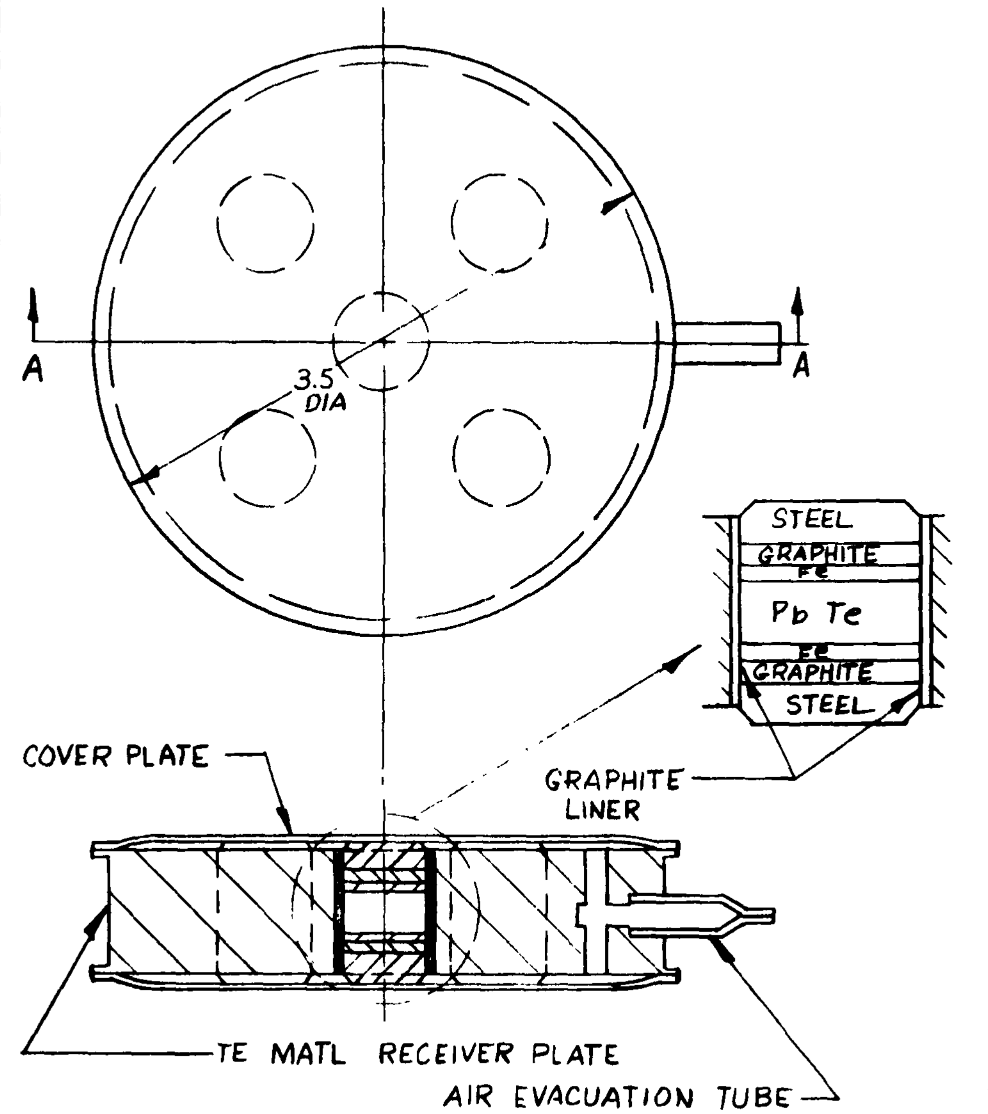
Extreme care will be exercised during assembly to remove surface oxides and in the selection of chemically compatible materials.

Unlike the original capsule technique where pressure was exerted on all exterior surfaces, pressure will now be applied to the ends of the elements only, with radial constraint provided by the material receiver walls.

In addition to bonding iron end caps to full cylindrical TE material elements, an attempt will be made to form P-N junctions and an assembled cartridge with the exception of the base seal.



Advance Engineering DECO - G.E. Co. Lynn, Mass.	FIGURE 4 TE Material Receiver Plate	Quarterly Report #5 Contract NObs 86854 D. J. Gibson 5/15/63



Advance Engineering DECO - G. E. Co. Lynn, Mass.	FIGURE 5 TE Receiver Plate Assembly	Quarterly Report #5 Contract NObs 86854 D. J. Gibson 5/15/63

It is believed that close control over process conditions will produce superior iron to telluride bonds without degradation in thermoelectric properties. Pressure will be held constant during the heating and cooling cycle to prevent the relaxation of elements in the assembly.

Tin Telluride Brazing studies have been conducted by the General Electric Advanced Technology Laboratory at Schenectady, New York, and at the Direct Energy Conversion Operation at Lynn, Mass. A brief summary of the results from these efforts follows.

The Tyco brazing technique was explored in detail with elements 1/4 inch in diameter and 1/4 inch long. Exploratory work with this geometry was conducted by A. T. L. Researchers there discovered that an initial r/ρ ratio of 0.06 - 0.05 cm could be obtained at operating temperatures. However, couple testing at design temperatures with temperature cycling resulted in the separation of the iron end caps from the SnTe.

A second attempt involving an improvement in material preparation to insure cleanliness and with temperature and time determined through experiment for the brazing operation resulted in what was believed to be the best possible bond. Again, couple operation at temperature with temperature cycling resulted in rapid degradation with each cycle. It is now believed that a systematic approach to the iron end cap bonding problem must involve an element geometry study to determine an acceptable length/area ratio and the evaluation of diffusion barriers which more closely match the coefficient of expansion of lead telluride.

Exploratory Tin Telluride brazing work at DECO has been restricted to the TE element geometries used in the cartridge (i.e. half cylinders with 1/2 inch diameter and a length of 1/4 inch). Again, almost negligible bond resistances were initially obtained with this technique. When these elements are fabricated into the cartridge and testing performed, rapid degradation accompanies temperature cycling.

A detailed examination of the failed cartridges has revealed that both iron end cap separation and cracks in the PbTe were responsible for the rapid degradation. This again clearly shows that coefficients of expansion between diffusion barriers and PbTe must be carefully matched.

Our continuing effort with SnTe brazing shall include an exploration of techniques to prevent iron end cap separation and that of lessening the stresses which result . element fracture.

I-2 Test and Evaluation

A total of 20 cartridges have been tested at the writing of this report. It is important to note that all units produced power initially and that there were no abrupt failures during operation at temperature. This would seem to indicate that when a fractured "P" or "N" element is subjected to the compressive load, applied through differential expansion, the electrical integrity of the package is maintained.

Cartridges, during testing, have been subjected to the same conditions as in a generator application. Heat is applied with an exposed natural gas flame. Sink temperature is monitored and accurately controlled, with heat rejection to a water sink.

Tabulated data on Pages 16, 17 and 18 show electrical resistance during cartridge fabrication, maximum power obtained and information pertinent to fabrication and degradation. Cartridge degradation has resulted from corrosion within the package, fracture during operation, and separation of iron end caps from PbTe. We have shown that corrosion may be eliminated by providing an inert atmosphere (argon), through selection of materials for chemical compatibility and by a hermetically sealed enclosure. The bonding of diffusion barriers has received primary attention and is considered to be the paramount problem in the fabrication of the unit.

TABULATED DATA WITH COMMENTS PERTINENT TO CARTRIDGE FABRICATION AND TEST EVALUATION

Cartridge No.	Length		Resistance (μΩ) As Received	After Bonding and Splitting	Junction	After Soldering	No. of Welds Base	End Cap	Max. Power (Watts)	COMMENTS
1	.500								0	Compressed assembly including 17 mil iron end caps. Exhibited continuity and generated current when placed on a hot plate but failed when tested (with torch).
2	.500	P N		1050 735		3000 950	1	3		Pin hole developed in weld - 3 attempts failed to close it - sealed with water glass - no performance data.
3	.500	P N		1035 750		3300 1200	1	2		End cap weld interrupted welding on second try. Used in demonstration unit.
4	.500	P N		800 605		2950 1125	1	1X	.65	30 mil copper used to shim 'P' leg. End cap weld bubbled; no heat sink used, sealed with cement. Tested at A. T. L.
5	.500	P N		970 495		2700 800	1	1	.73	Copper shim under 'P' leg. Base weld good, appearance fair, end weld very good. Thermocouple in hot junction to monitor temperature
6	.500	P N				2975 1150	2	1	.72+	The elements were washed thoroughly to remove flux and prevent corrosion. Welding was done in a bell jar with an argon atmosphere. Performance - initially .71 W, cartridge-sink joint failed at 235 hours; after resoldering, P = .72 W. Therefore, initial power was higher. At 1000 hours P = .54 W; at 2000 hours and 50 thermal cycles, P = .40 W. Base welded twice, end cap OK on first try.
7	.500	P N				2500 1450	1	1	.62	Fabricated same as #6 except: (1) water glass on elements to prevent corrosion - N.G. - water glass flaked off. (2) sheet mica with a different binder used as insulator - N.G. - the binder carbonized at operating temperature. Performance - .20 W initially, .62 after 47 hours, 0+ at 167 hours. Silver shim on hot side shifted during assembly leaving poor contact and increased electrical and thermal impedance. Welded in bell jar, both welds OK on first try.
8	.500	P N		500 450	before splitting	3940 1560	1	2	.89	Solder joint washed thoroughly - 35 mil silver disc used as buffer at hot junction. Base weld OK, end weld OK on second try. Performance - .89W initially, .86 at 60 hours, degraded rapidly to 0+ after this. Thicker silver disc had sublimed quite a bit, increasing thermal impedance.
9	.500	P N		500 450	before splitting	4800 1560	1	1		Both welds excellent on first try. Solder bridged elements at cold junction during sink attachment. Elements broke while disassembling to repair. No performance data.
10	.500	P N		500 625	before splitting	9500 1260	*(2)	1	.51	* (Fixture motor burned out during first weld.) Circuit continuity check showed 90Ω resistance before test. Voltage but no current for first 20 minutes. Hot end insulator was off center 30 mils causing the silver buffer to "cock." Although the base was flushed thoroughly after soldering, a heavy accumulation of rust was noticed at the cold end.

TABULATED DATA WITH COMMENTS PERTINENT TO CARTRIDGE FABRICATION AND TEST EVALUATION

Cartridge No.	Length		Resistance (μΩ) As Received	Resistance (μΩ) After Bonding and Splitting	Resistance (μΩ) Junction	Resistance (μΩ) After Soldering	No. of Welds Base	No. of Welds End Cap	Max. Power (Watts)	COMMENTS
11	.500	P				2050	1	2	.99	Two 5 mil silver discs used to bridge hot end as 35 mil silver seemed unsatisfactory (high yield and sublimation rate). This is the first cartridge welded in the Hydrovoid Box. Performance - .99 initially with 14% degradation during 170 hours. From then until 2000 hours, degradation proceeded at the rate of 1.4% per 100 hours. There were 50 thermal cycles. The first two affected it but succeeding ones did not. Ten cycles imposed on the cartridge within 4 hours (after 1700 hours of life) did not affect the rate of degradation. Power at 2000 hours - .60 W. Disassembly - Removal of hot side assembly showed very little oxide on the heat transfer surfaces. The silver was discolored (black) only near the edges. 50% of the area of the iron end cap had retained its original luster, and the elements were discolored only at the cold end (due to the soldering operation). There was no trace of the red oxide usually found on the cold junction. A 1/8" wide band of PbTe had condensed on the mica insulation. Since everything is in fairly good condition, the degradation rate of 1.4% per 100 hours over the last 1800 hours of life could be attributed to a continual hot junction temperature of $1250^{\circ}F+$ (see cartridge no. 18).
		N				1500				
			At disassembly, the 'N' had a resistance of 8700 μΩ, 'P' = 27,700 μΩ. The hot side end cap of the 'P' fell off (bonded only near the edge) and element plus cold end cap resistance was only 4250 μΩ.							
12	.500	P				3850	2	1	.89	The hot side assembly was brazed, the only contact joint in the stack-up was between the iron end caps and the silver buffer. This cartridge went 2000 hours with a final power output of .32 watts. Before final assembly, the 'P' leg was chipped on both corners and had a large peripheral crack which explains a higher degradation rate than No. 11. Disassembly showed fracture of the 'P'.
		N				950				
			(after disassembly N = 1275 μΩ, P = 55,100 μΩ)							
13	.300	P		1060		10,500 Total	3	2	.64	This is the first cartridge to have sheet iron diffusion barriers brazed on with SnTe. A disc of iron was used as both diffusion barrier and hot junction. Performance - Thermal impedance initially was very high. Thermal impedance increased and electrical impedance decreased with time over the next 2 hours until electrical impedance was 1/2 its initial value. A black deposit had formed on the silver buffer increasing thermal impedance. The SnTe bond was still intact on the hot side as deliberate removal of the end caps caused the separation to occur in the PbTe. Only 20% of the 'N' cold junction was wetted by SnTe.
		N		780						
14	.342	P		1420	190	1580	1	2	.96	A pin hole developed in the end cap weld. Re-welding failed to close the hole so it was tested as is. Thermal impedance increased with time and output decreased. Being exposed to the atmosphere probably caused a material degradation.
		N		1020	15	1280				
15	.353	P		765	70	925	3	1	1.05	Hot pressed powdered iron on 'P' leg, SnTe brazed sheet iron on 'N' leg. Performance degradation - 12% the first 100 hours, 2% the second 100 hours, 6% per 100 hours over the next 300 hours. At 500 hours, two $80^{\circ}F$ overshoots in temperature within 30 hours. Performance decreased 10% over the next 100 hours and the rate increased so that power was 0.16 watts at 1000 hours.
		N		1320	95	1590				

TABULATED DATA WITH COMMENTS PERTINENT TO CARTRIDGE FABRICATION AND TEST EVALUATION

Cartridge No.	Length		Resistance ($\mu\Omega$) As Received	Resistance ($\mu\Omega$) After Bonding and Splitting	Resistance ($\mu\Omega$) Junction	Resistance ($\mu\Omega$) After Soldering	No. of Welds Base	No. of Welds End Cap	Max. Power (Watts)	COMMENTS
16	.289	P		1300	280	1695	3	2	.81	SnTe brazed sheet iron on a 'P' type Trancoa leg, SnTe brazed sheet iron on 3M 'N' leg. After three hours of operation, higher temperatures were needed to maintain design voltage showing a shift in the hot side assembly. The silver buffer sublimed, reducing the cross-sectional area of the hot strap resulting in increased electrical impedance.
		N		995	55	1125				
17	.232	P		900		1090	3	2	1.12	Hot strap was a solid iron end cap, topped with two 5 mil silver discs. Initial output of 0.115 V x 9.7 A = 1.12 watts degrading to almost zero after 120 hours. Disassembly showed sublimation of silver leaving only a spot in the center of the cartridge approximately 1/4 the original area of <u>one</u> disc. Three end caps broke at the SnTe junction. The 'P' leg had a total resistance of 24,000 $\mu\Omega$, the drop across the one end cap and SnTe being 8,400 $\mu\Omega$ of it. The 'P' leg had a resistance of 8,700 $\mu\Omega$ (no end caps). A check of Seebeck voltage showed the material was satisfactory in this respect. Base seal was not gas tight after operation.
		N		960		1090				
18	.260	P	425	960		(1) (2) 2100	1	1	0+	Solid iron hot strap/diffusion barrier. Solder did not "take" on first attempt; second attempt caused 'P' leg resistance to double. This cartridge had thermocouples at the hot junction and at both cold junctions. Performance was very poor, current only 0.1 amp. When the hot junction was 1100°F, the cold junction was 306°F which was higher than expected. The O.C.V. was 0.207 volts vs. the design O.C.V. of 0.230 volts; the hot junction temperature had to be increased to 1268°F which caused cold junction temperature to become 340°F. Failure is attributed to severe cracking of the 'P' leg. Poor sink attachment caused high electrical/thermal impedance.
		N	400	1125		(1) (2) 1325				
19	.260	P	225	875		1125	3	1	1.01	Two pieces of 5 mil silver as hot strap. Performance - required 150°F range of adjustment on end cap to maintain design O.C.V. of 0.230 V showing shifting of the hot side assembly. High rate of increase of resistance could be due to thermal stresses imposed by the shifting hot side assembly.
		N	320	1000		1150				
20	.242	P	290	1150		1475	3	4	.62	Solid iron hot strap/diffusion barrier, no buffers. A hole developed in the end cap weld; removed cap and welded new cap in place - holes still there (contaminated sleeve?). Performance - Since initial output was only 0.62 watts and there were holes in the hot end, the cartridge was run less than two hours. Disassembly showed a large accumulation of rust on cold iron end caps equal to 70% of accumulation of cartridges run for longer periods. Therefore, the oxide must be due to oxygen entrapment at assembly rather than base seal leakage. The metallized surface of the beryllia insulator nearest the hot junction "disappeared."
		N	375	995		1410				
21	.242	P		825		1100				Serrated iron end caps on hot end. One section of one cap broken off (approximately 20% of area). Not assembled.
		N		790		890				
22	.242	P		1265		1620	3	2		Silver hot strap. Hole in end cap weld; tried filling with braze but hole remained.
		N		710		810				
23	.270	P	250	1420		1675	1	1		Split end cap, silver bridge. Sleeve and end cap were pickled in a solution of H_2O, nitric and hydrofluoric acids for pre-weld cleaning. This appears to alleviate welding problems. Finned surfaces were attached for display purposes. It was tested at low temperatures to avoid large thermal stresses. Power = 0.030 volts x 3.84 amps = 0.105 watts, internal resistance = 7800 $\mu\Omega$.
		N		925		1160				

It was believed that the isostatic bonding of iron end caps would provide TE material densification approaching that of a single crystal and thereby improve its resistance to fracture. Material processed initially in the autoclave was not suitable for fabrication in the cartridge due to the very high resistance in "P" type elements.

SECTION II - RECOMMENDATIONS FOR FUTURE CARTRIDGE DEVELOPMENT

The development effort described below is aimed at solving problems encountered in cartridge fabrication. Since the cartridge method of material containment is mechanically sound and offers distinct advantages over other assembly methods, it must be explored in greater detail with emphasis on principal problem areas. Problem areas requiring continued exploration are the mechanical behavior of lead telluride and the bonding of diffusion barriers having low electrical resistivity combined with good mechanical strength.

II-1 Improved Lead Telluride

Metallographic sections of commercial PbTe thermoelements always reveal the presence of numerous small voids, micro-cracks and segregated phases in the grain boundaries. Because of these defects, commercial lead telluride as it is presently manufactured is considerably more brittle than the ideal polycrystal would be.

A study must be conducted to investigate the behavior of the lead telluride whose crystalline state approaches that of an ideal polycrystal more nearly than that of currently available commercial materials. The most promising method for producing such material appears to be casting with ultrasonic agitation of the melt during freezing.

Isostatic bonding results to date have shown that densities nearly equal to theoretical single crystal density may be obtained with this technique. This effort should, therefore, be continued in an attempt to improve PbTe mechanical properties through increased densification.

II-2 Minimization of End Constraints

Methods of minimizing the stresses due to end constraints on PbTe elements will be explored in detail. The following approaches will be investigated:

1. Iron end caps will be split by methods that will remove the constraints introduced by solid caps, either through dicing or fabricating the end caps from a tightly wound spiral of iron strip.

2. Materials whose thermal coefficient of expansion matches that of PbTe shall be explored and tested.

II-3 Ceramic Insulators & Seals

The use of ceramic materials will be investigated in the following areas:

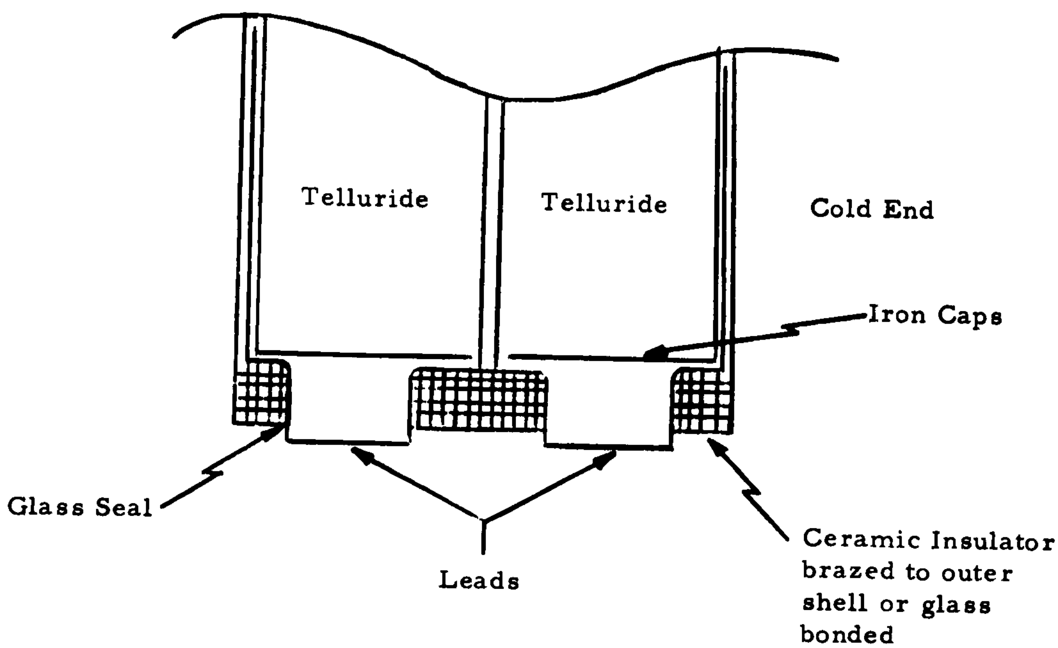
1. Hot side assembly.
2. Cold side seal.
3. Inside wall insulation.

The hot side assembly is relatively simple since there are no leads to press through the shell at the end of the cartridge. The program will consist in finding or developing a suitable high temperature insulating adhesive for bonding iron to the inconel cap. A satisfactory adhesive would greatly diminish the temperature gradient at the hot side and simplify the assembly procedure.

The cold side seal is complicated by the necessity for making high current lead connections at the end of the cartridge. Several approaches are being considered which offer promise, but all of them will depend on effecting a bond with material having good thermal conductivity.

Ceramic to metal seals are better in strength and electrical insulation than ceramic to glass seals. The ceramic to metal seal, however, is usually difficult and costly to make. Figure 6 represents a concept in combining ceramic to metal sealing with glass bonding. Several variations will be evaluated.

Figure 6



Telluride
Telluride
Cold End
Iron Caps
Glass Seal
Leads
Ceramic Insulator
brazed to outer
shell or glass
bonded